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(54) Title: **METHOD FOR SURFACE PATTERNING USING A FOCUSED LASER**

(57) Abstract: A method for direct micropatterning of a surface by laser irradiation comprises: (i) covering a surface with a sample comprises either a homogeneous solution of one or more soluble metal salts, or a solution or suspension of a metal-ion containing compound of type A; (ii) irradiating the surface locally by applying a focused laser beam, thus resulting in local deposition of either (a) a metal(s) or metal oxide(s) obtained from the decomposition of the metal salt(s) from said homogeneous solution, or (b) a metal-ion containing compound of type B obtained from the decomposition of the initial type A compound from said solution or suspension; and (iii) repeating step (ii) by moving either the laser or the sample thus creating spots or lines of the deposited metal(s) or metal oxide(s), or compound of type B. By this method patterned lines of silver and modified or capped silver, gold, copper oxide and molybdenum disulfide were obtained.

## METHOD FOR SURFACE PATTERNING USING A FOCUSED LASER

### Field of the Invention

The present invention relates to a method for direct micropatterning of surfaces by  
5 laser irradiation and to micropatterned surfaces thus obtained.

### Background of the Invention

The ability to localize chemical reactivity to predetermined sites elicits a broad  
spectrum of interest and applications. In particular, chemical patterning of surfaces at the  
10 micron scale, and below, lies at the basis of many emerging technologies.

Mask-based photolithography techniques adapted from the microelectronics  
industry are the current standard. Exposure of a photosensitive layer to the illuminated  
pattern determines the fate of the surface beneath it, typically for removal or modification.  
Consecutive chemical operations may be achieved by multiple steps. An elegant example is  
15 light directed chemical synthesis (Fodor et al., 1991) where solid-phase chemistry,  
photolabile protecting groups and photolithography have been combined to achieve a  
highly diverse surface. Light-directed synthesis of oligonucleotides is at the heart of many  
DNA chip technologies, and a similar approach has been applied to arrays of peptides  
(Grebel et al., 1990; Goffeau, 1997) . However, the lithographic methods suffer a number  
20 of disadvantages, particularly in the complex instrumentation required to produce and align  
the masks reliably. Moreover, the dependence on photosensitizers may limit the choice of  
compatible materials.

Other methods for localizing chemical reactivity include micro-contact printing (Xia  
et al., 1996; Xia et al., 1997) direct deposition by micropipets or "ink jet" technologies, and  
25 electrochemical deposition using scanning probe microscopes (Schoer et al., 1994; Maoz et  
al., 1999).

Photochemical interactions of a 360-514 nm laser beam with a colloidal suspension  
of several precursors were utilized for generating patterns of cadmium and selenium (Weiss  
et al., 1992; Peled et al., 1992a). A holographic relief grating was produced by recording  
30 the interface pattern of two coherent laser beams (Peled et al., 1992b; Weiss et al., 1994).

Localized absorption of heat in a thin gold film irradiated by a focused infrared laser  
can etch the film. Colloids suspended in solution above such a film may be entrained in a  
convective flow and brought to stick to the etched pattern. Where the colloids are coated  
with biomolecules, micro-arrays of DNA, peptides, or proteins may be produced

(Shivashankar and Libchaber, 1998). In all these methods a modified surface is left, though they differ in the essential manner that localization may be achieved either by restricted delivery of a reagent, or by localized reaction in a homogeneous medium induced by some external probe.

5           The key point to all these methods is gathering functional molecules at the surface, followed by their manipulation to form specific chemical sites in predetermined patterns. Difficulties of producing such well-defined microstructures accompany the multistep lithographic process, e.g. creation of a homogeneous lithographic or photolithographic mask or a stable monolayer with minimum hole-like defects, reproducibility of such  
10 substrates, and reaction only at preselected sites and not in arbitrary architectures.

### **Summary of the Invention**

It has now been found, according to the present invention, that microscale-patterned surfaces can be generated simply by applying a tightly focused laser beam directly on a  
15 homogeneous solution containing soluble metal salts or on a suspension containing a metal compound. When focused laser beam is applied onto a homogeneous solution containing soluble metal salts, decomposition occurs leading to the corresponding metal or metal oxide. When focused laser beam is applied onto a suspension containing a metal compound, decomposition occurs leading to a different compound of said metal.

20           The present invention thus relates to a method for direct micropatterning of a surface by laser irradiation, which comprises:

(i) covering a surface with a sample comprising either a homogeneous solution of one or more soluble metal I salts, or a solution or suspension of a metal II-compound A;

(ii) irradiating the surface locally by applying a focused laser beam thus resulting in  
25 local deposition of either (a) a metal(s) I or metal I oxide(s) obtained from the decomposition of the metal I salt(s) from said homogeneous solution, or (b) a metal II-compound B obtained from the decomposition of the initial metal II-compound A from said suspension; and

(iii) repeating step (ii) by moving either the laser or the sample thus creating spots  
30 or lines of the deposited metal(s) I, metal I oxide(s) or metal II-compound B.

As used herein in the specification, the term "metal of type I" (metal I) refers to a metal ion from whose soluble salt the method of the invention will produce a deposition of the reduced metallic or oxide form, while "metal of type II" (metal II) refers to a metal ion

from which the method of the invention will produce a molecular compound that differs from that of the starting material.

Any hydrophilic or hydrophobic surface may be used for attachment of the deposited metal, metal oxide or metal compound. Examples of hydrophilic surfaces include, but are not limited to, borosilicate glass, quartz glass, or glass modified by tetraethylorthosilicate (TEOS), passivated silicon or modified polymer surfaces, provided that the laser wavelength is selected such that it is not absorbed by the substrate. Examples of hydrophobic surfaces include, but are not limited to, glass modified by octadecyltrichlorosilane (OTS) or poly (methyl methacrylate) (PMMA).

In one embodiment, the sample comprises a homogeneous solution of one or more metal I salts. The metal I salt may be, for example, a soluble salt of a metal I selected for electrical conductivity. In another embodiment, the metal I serves as a base for local adsorption or for modification by other chemical species.

Examples of such soluble metal I salts include, but are not limited to, salts of Ag, Au, Pb, Ni and Cu. Thus, in one embodiment the deposited metal I is silver that may be obtained from decomposition of  $\text{Ag}(\text{NH}_3)_2\text{OH}$ . The deposited Ag may be further reacted with other chemical species such as hydrobromic acid thus resulting in a similar line of AgBr or with dithiothreitol, thus resulting in a similar line of Ag complexed with sulfur.

In another embodiment the deposited metal I is gold that may be obtained from decomposition of  $\text{NaAuCl}_4$ .

In a further embodiment the deposited metal I oxide is copper oxide, that may be obtained from decomposition of  $\text{Cu}(\text{NH}_3)_2\text{OH}$ . The deposited copper oxide may be further reacted with dopants thus resulting in high temperature doped copper oxide superconductors. In an alternative, mixtures of copper salts and salts of the dopant materials are exposed to the laser beam resulting in simultaneous deposition of the copper oxide in association with the dopants. For example, suitable copper salts may be mixed with suitable salts of elements including, but not being limited to, La, Y, Sr and Ba. In this way, direct deposition of mixed or doped patterns may be achieved, including those suitable as high temperature superconductors.

In another embodiment, the sample comprises a suspension of a metal II-compound A that decomposes to a different metal II-compound B. The is preferably a transition metal such as Mo, W, V, Zr, Hf, Pt, Re, Nb, Ta, Ti and Ru, preferably Mo and W.

In one embodiment, the deposited metal II-compound B is  $\text{MoS}_2$  that can be obtained by decomposition of the metal II-compound A  $(\text{NH}_4)_2\text{MoS}_4$ . In another embodiment, the deposited metal II-compound B is  $\text{WSe}_2$  that can be obtained by decomposition of the metal II-compound A  $(\text{NH}_4)_2\text{WSe}_4$ .

5 According to the invention, the solution is activated in a small volume predetermined by the laser's focus, which defines a "reactor volume". The desired product precipitates and consequently patterns the substrate in a local region on the surface. The width of the laser spot, determined by the focusing objective, dictates the size scale of the pattern generated on the surface. In one embodiment, the laser is focused to 0.5 micron  
10 width and the resulting patterns have typical width from 3 to 8 microns depending on the material and conditions.

The method of the present invention offers a number of advantages over conventional lithography for selected applications, in two categories. First, the method is suitable for a broad spectrum of materials, including those not suitable for evaporation or  
15 sputtering through a mask. Second, as a direct-write technique, it avoids the necessity of producing a mask for photoresist activation and thus may be applied quickly for prototype production, as well as the marking of sample-specific labels such as serial numbers or codes. The focus on chemical activation of homogeneous solutions using localized laser irradiation is entirely novel.

20 The patterns can be modified chemically after production, keeping the original pattern unchanged. Mixtures of materials may also be deposited directly. The demonstrated formation of copper oxide patterns leads directly to application in circuitry based on high-temperature superconductors, all of which are based on doped copper oxide. Applications to screening sensors of biomolecules or other chemical species are feasible based on  
25 construction of arrays binding specific reagents at predetermined locations.

### **Brief Description of the Drawings**

**Figs. 1a-1e** depict characteristics of silver (Ag) lines. 1a) Scanning electron (SE) micrograph and 1b) optical image of Ag lines; Lines width varies from 6-10 microns and  
30 their morphology is characterized by very thin leaf like microstructures. 1c and 1d) analyses of points 1 and 5, respectively, as examined by EDS, of the Ag line of Fig. 1a spectrum of Ag line (point 1) indicates that lines are composed of pure Ag, while nearby the line (glass) (point 5) composition is primarily of Si and O. 1e) Ag lines are continuous

and electrically conductive. Current-voltage plot of Ag line shows linear dependence typical of metals.

**Figs. 2a-2e** depict characteristics of modified Ag lines. 2a) Analysis of AgBr line by EDS. 2b) SE micrograph of Ag-DTT line. In contrast to pure Ag lines, the morphology consists of densely-packed submicron spheres. 2c) SE micrograph of Ag-PVP grown by the “fast” mode involving heat liberation, at high laser intensity. Note the craters left by explosive formation of vapor bubbles. 2d) SE micrograph of Ag-PVP grown by the “slow” mode at low laser intensity. 2e) optical image of lines formed in the “slow” mode showing the range of widths from 0.7 to 4 microns. Lines in panels a and b are conductive; those in c and d are not.

**Figs. 3a-3b** depict characteristics of gold (Au) lines. 3a) Optical micrograph of deposited Au line of 3-4 micron width. 3b) Analysis of Au line by EDS.

**Figs. 4a-4b** depict characteristics of copper oxide lines. 4a) Optical micrograph of deposited copper oxide line of 4 micron width. 4b) Analysis of copper oxide line by EDS.

**Fig. 5.** Scanning electron micrographs of MoS<sub>2</sub> line. Line width varies from 3.5 to 7 microns, depending on laser intensity. MoS<sub>2</sub> patterns are characterized by porous, spongy morphology.

### **Detailed Description of the Invention**

The present invention provides a method for generating microscale-patterned surfaces simply by applying a tightly focused laser beam usually used as optical tweezers (Ashkin et al., 1986) directly onto a homogeneous precursor solution containing soluble reagents. In practice, the solution is enclosed by a glass slide and cover slip separated by wax spacers. The laser is introduced to the optical path and focused by the imaging objective of a microscope. The laser radiation passes through the glass slip and strikes the solution at the interface, inducing the chemical reaction to start and propagate. Importantly, the reaction takes place only if the laser is focused directly at the glass-solution interface. Defocused light, or focusing within the solution has no apparent effect. The reaction volume is thus confined by the optical focus of the laser. The product deposits as a solid, usually with a great liberation of heat, and attaches firmly to the surface. Operating the laser momentarily forms isolated spots, while moving the microscope stage or the laser spot in the x-y plane draws continuous lines.

Several products have been patterned by the direct laser deposition method of the invention. They differ in chemical composition, feature size (0.7-10 microns), electric and

thermal conductivity, morphology, and microstructure. These characteristics depend on the precursor solution, added capping agents, laser beam intensity and drawing velocity. The laser in use is a solid-state laser diode of 830 nm wavelength and 200 mW maximum output.

5           Direct-write surface patterning from solution according to the invention will find application in diverse fields. These will take advantage of several features of the method, including the flexibility of materials choice, the ability to combine local pattern formation with specific chemical functionalization (either during production of the pattern or afterwards), and the control on morphology of the final product.

10           Direct-write patterning is ideal for sample-specific marking, such as serial numbers, codes, security codes, and identification cards. Taking advantage of the ease to change the deposited material simply by exchanging a precursor solution, identifying patterns could be produced which incorporate compositional encoding that would be difficult to duplicate.

          The method of the present invention is suitable for production of base substrates for  
15   combinatorial chemical or biochemical arrays. These may include specific oligonucleotide arrays ("DNA chips"), antibody arrays, peptide arrays, arrays exposing specifically functionalized polymers (natural or synthetic or a combination thereof), and arrays of small functional molecules bound to the micropatterned structure. For example, a silver or gold pattern could be produced and functionalized by thiol or amine reagents. Arrays may be  
20   built by serial production of a local pattern (e.g. dot or line) and its functionalization, either during or following the pattern formation as described. The functionalizing solution would be exchanged and the next formed pattern functionalized by a different reagent.

          The surface functionalization of continuous metal or semi-conducting patterns according to the invention also permits the detection of complexation involving charge-  
25   transfer between the immobilized species and another species from solution or vapor phase. Similarly, charge-transfer functionalization can be used to produce light-detecting elements. The functionalized lines will also be useful for localized electrochemical reactivity, for example in the production of micron-sized batteries for microelectronic devices.

          The flexibility of suitable starting reagents permits deposition of junctions of  
30   dissimilar materials (e.g. thermocouples), as well as alloys and mixtures of mutually insoluble materials. In this vein, the deposition of Cu in oxide form, with great liberation of heat immediately suggests other ceramic composites, which are not easily patterned at the micron-scale by conventional evaporation or sputtering methods. These could include the

doped copper oxide high-temperature superconductors such as, but not limited to, YBaCuO.

The deposition of transition metal compounds demonstrates a new feasibility for direct-write patterning with non-metallic materials at the micron scale. MoS<sub>2</sub> in particular is semi-conducting. MoS<sub>2</sub> and other semi-conducting compounds could find application in micro-electronic circuits and devices. The combination of such semi-conductors and metal patterning is straightforward, as are electronic devices based on junctions between dissimilar semi-conducting compounds, including rectifiers, transistors, and light detectors.

The deposition of MoS<sub>2</sub> can reasonably be extended to a broad class of materials including, but not being limited to, other transition metal chalcogenides such MoSe<sub>2</sub>, MoTe<sub>2</sub> and analogous compounds of tungsten. In general, the conditions of such a reaction are that the elements of an insoluble metal-ligand compound be contained within an ionic complex, such as having an excess of the ligand balanced by cation species such as ammonium. Thus, if the starting material is (cat)<sub>m</sub> M X<sub>n</sub>, wherein M is a multivalent metal ion, X is a ligand, cat is a cation such as NH<sub>4</sub> and the number of cations is such that it should equal the difference between the total charge of the ligands minus the valence of the metal ion. The product of decomposition of said starting material would be M X<sub>n-m</sub>. For example, as shown herein, when the starting material is (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> the product of decomposition is MoS<sub>2</sub>. In the same way, when the starting material is (NH<sub>4</sub>)<sub>2</sub>WSe<sub>4</sub> the product of decomposition is WSe<sub>2</sub> and when the starting material is 2(NH<sub>4</sub>)PtCl<sub>6</sub> it can decompose to PtCl<sub>2</sub> + 4(NH<sub>4</sub>)Cl or to PtCl<sub>4</sub> + 2(NH<sub>4</sub>)Cl.

The invention will now be illustrated by the following non-limiting Examples.

## EXAMPLES

### Experimental

Optical observations were made by Nomarski differential interference contrast (DIC) microscopy (Zeiss optics, Fluar objective 100x N.A. 1.3) and a digitally enhanced 0.5 in. CCD camera (iSight iSC-2050LL). A single-mode diode laser operating at 830nm, 200mW maximum output power (SDL-5432, SDL, Inc.) was introduced to the optical path using a dichroic mirror. The sample cell consisted of a long cover slip (22x40 mm, No 1.5 thickness) fixed crosswise to an ordinary glass microscope slide (25x76 mm) using wax spacers, leaving final dimensions approximately 5x25x0.1 mm.



Scanning electron microscopy was performed in a JEOL GMC 6400 equipped with an Oxford Link EDS spectrometer. Samples were prepared by breaking open the cell described above, and coating with a thin film of carbon.

The following solutions were subjected to laser irradiation to form Ag, Au CuO and MoS<sub>2</sub> patterns:

a. Diamminesilver hydroxide solution

The solution was prepared by mixing equal volumes (0.5 ml) each of 10% silver nitrate (AgNO<sub>3</sub>) aq. solution and 10% sodium hydroxide (NaOH) aq. solution. The heavy precipitation of silver oxide (Ag<sub>2</sub>O) was dissolved by adding dropwise an aq. solution of ammonium hydroxide (1.5-1.8 ml, 2.5%), and the resulting clear solution was passed through a 0.2 micron filter and injected to the sample cell.

b. Sodium tetrachloroaurate

The solution was prepared by adding 300 microliters of aq. sodium carbonate (50mg/1 ml) to aq. solution of gold tetrachloride acid trihydrate (30mg. /400 microliters). The resulting solution (pH 8) was diluted with an equal volume of water passed through a 0.2 micron filter and injected to the cell sample.

c. Diamminecopper hydroxide solution

The solution was prepared by dissolving copper sulfate pentahydrate (CuSO<sub>4</sub>5H<sub>2</sub>O, 1.5 gr.) together with sodium chloride (NaCl, 0.5 gr.) in hot water (6 ml), and adding to a solution containing sodium bisulfite (NaHSO<sub>3</sub>, 0.5gr.) in 5 ml 5% sodium hydroxide aq. solution. The white precipitation of cuprous chloride was washed with water by decantation, dissolved by ammonium hydroxide aq. solution (10ml, 25%), passed through a 0.2 micron filter, and injected to the sample cell.

d. Ammoniumtetrathiomolybdate solution

A red-brown clear solution, prepared by dissolving ammonium tetrathiomolybdate (Aldrich) to form 5 mM solution, was filtered through a 0.2 micron filter and injected to the sample cell.

### **Example 1. Silver (Ag) patterns**

The technique of the invention was first demonstrated by operating the laser on a solution of diamminesilver hydroxide (Tollens' reagent) Ag(NH<sub>3</sub>)<sub>2</sub>OH (Vogel, 1989) using borosilicate glass as the patterned substrate.

A solution of Ag(NH<sub>3</sub>)<sub>2</sub>OH was prepared by mixing equal volumes (0.5 ml) each of 10% silver nitrate (AgNO<sub>3</sub>) aq. solution and 10% sodium hydroxide (NaOH) aqueous

solution. The heavy precipitation of silver oxide ( $\text{Ag}_2\text{O}$ ) was dissolved by adding dropwise an aqueous solution of ammonium hydroxide (1.5-1.8 ml, 2.5%). The resulting clear solution was passed through a 0.2 micron filter and injected to the sample cell consisting of a cover slip fixed crosswise to an ordinary glass microscope slide separated with spacers, and mounted on a microscope stage. A laser was introduced to the optical path and focused by the imaging objective of the microscope. The laser radiation passed through the glass slip and activated the reagent in the solution to form a crystalline droplet of metallic silver that deposited and attached firmly onto the glass surface. Isolated spots were formed by operating the laser momentarily, while continuous lines were drawn by moving either the microscope stage or the laser spot.

The lines, squares or other desired shapes were of metallic silver (Ag), roughly 8 microns in width and 1.5 microns in height. The formation of a silver spot occurs when the microscope stage and the laser beam are not moving. If the laser focus is left stationary, the silver deposit expands steadily to form a disk that may reach 50-60 microns diameter. A narrower line is formed when the microscope stage or the laser spot is moved. Addition of capping agents modifies the dimensions, morphology and conductivity as described below. The formation of the deposit is usually accompanied by the production of vapor bubbles detected by a video camera.

Substrates with various surface modifications were tested for the deposition process. Surfaces such as borosilicate glass, gold coated borosilicate glass, quartz glass, glass modified by tetraethylorthosilicate (TEOS), by octadecyltrichlorosilane (OTS) or by poly(methyl methacrylate) (PMMA), have been used. The major difference was in the adhesion of the silver pattern to the substrate. Borosilicate yielded the strongest adhesion, while deposits on OTS or PMMA coated glass were often unstable even during the process, and it was not possible to generate continuous lines. On these substrates the deposit was often ejected from the surface immediately by the accompanying vapor bubble, or just after rinsing the substrate glass with water from the precursor solution.

When the line was removed, either mechanically by sonication or chemically with nitric acid, local etching of the borosilicate solution glass substrate was seen in the SEM. This suggests very intense heating, consistent with significant absorption of the laser radiation by the deposit. The etching is consistent with the firm attachment of the silver to borosilicate glass, as well as to glass coated by gold and TEOS. Quartz substrates were not etched due to their high melting point, and the attachment of the silver pattern to them was weaker than to borosilicate glass.

Morphology of thin leaves throughout the Ag deposit resulting from diamminesilver hydroxide solution is revealed by the scanning electron microscope (SEM). Energy dispersion spectroscopy (EDS) indicates an elemental composition of pure silver. A current-voltage plot shows the linear Ohmic relation typical of metals. These results are summarized in **Figs. 1a-1e**. All of this evidence confirms that the pattern is indeed composed of metallic silver.

**Figs. 1a and 1b** depict, respectively, scanning electron (SE) micrograph and optical image of Ag lines; Lines width varies from 6-10 microns and their morphology is characterized by very thin leaf like microstructures. **Figs. 1c and 1d** depict, respectively, EDS spectrum of Ag line (point 1) and (point 5), indicating that lines are composed of pure Ag (point 1), while nearby the line (point 5) the composition is primarily of Si and O. **Fig. 1e** Ag lines are continuous and electrically conductive. Current-voltage plot of Ag line shows linear dependence typical of metals.

## **Example 2. Modified silver patterns**

Pre-formed patterns may be further modified by chemical reaction. The broad leaf-like morphology allows the reagent to penetrate deeply into the structure and permits nearly complete conversion of the silver.

Silver lines were subjected to further chemical modification. For example, reaction of the silver line with 10% hydrobromic acid in aqueous solution for 2 minutes formed a silver bromide (AgBr) line. As expected, this line was not electrically conductive. **Fig. 2a** shows elemental analysis of the AgBr as examined by EDS and confirms the presence of Br atoms within the silver line. In addition, a clear change in morphology was observed.

In another experiment, incubation of the silver line with 8 mM threo-dithiothreitol (DTT, Cleland's reagent  $\text{HSCH}_2\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{SH}$ ) in ethanol for 24 h at room temperature, formed a new line of a silver-sulfur complex (Bain and Whitesides, 1989) that withstands the extensive washing with ethanol. Again, EDS analysis indicates the presence of sulfur, and the morphology changes significantly (not shown).

The reaction of the silver line with a dithiol as DTT or with other bifunctional molecules such as diamines and disulfides opens the possibility of reacting a bifunctional molecule for further binding of organic or biomolecular species to the original pattern. The high surface area provides an advantage over evaporated or sputter-deposited films for density of functionalization.

Another possibility of modification of the silver lines consists in the use of capping agents that enable to control the morphology of the deposited patterns and further provides a basis for organic chemical modification of the patterns. This technology can also be used for deposited gold patterns. Examples of capping agents that can be used both for silver and gold include, without being limited to, organic soluble thiols such as stearylthiol and DTT, soluble disulfides, soluble secondary and primary amines, soluble polymers such as polyvinylpyrrolidone (PVP), soluble surfactants, and the like.

In order to achieve some control over line characteristics and generate finer silver patterns, capping agents were added to the precursor diamminesilver hydroxide before operating the laser beam. They are commonly used in preparing size-limited silver colloids by stabilizing the initial nucleates (Korgel and Fitzmaurice, 1998). Addition of 0.1% (wt/wt) DTT to the precursor solution reduced the line width to 3-4 microns. The line morphology is an aggregate of small spherical crystallites of about 100 nm diameter, rather than broad thin leaves (**Fig. 2b**). EDS analysis did not reveal sulfur, suggesting that the capping agent was washed out by rinsing with ethanol.

Polyvinylpyrrolidone (PVP, with average M.W. of about 10,000) is another effective capping reagent for silver colloids in suspension (Huang et al., 1996). Its use at 0.5-1% (wt/wt) concentration resulted in two modes of patterning. At higher laser intensities the deposition proceeded rapidly and was accompanied by vapor bubble formation, as in the cases described above. The lines had typical width in the range of 4 microns with morphology of elongated silver crystallites larger than 100 nm, intermediate between pure Ag and the case of Ag capped with DTT (**Fig. 2c**). EDS analysis showed traces of nitrogen from the PVP capping agent together with silver, and such lines were electrically conductive. At lower laser output a second mode appeared. In this case the deposition was very slow and proceeded without vapor formation or other evidence of heating. Line widths as narrow as 0.7 microns were obtained in this mode. The EDS again showed Ag with evidence of nitrogen. Lines formed in this way were not electrically conductive, although they were rinsed thoroughly with ethanol both before and after prolonged incubations with water. Effective capping by the PVP apparently inhibits electrical conductivity between the small silver grains. This is consistent with the lack of Joule heating by the laser. It is known that sufficiently small metal colloids do not absorb focused laser radiation in the configuration of optical tweezers, and are even trapped at the focus by dielectric effects (Svoboda and Block, 1994). In this case the grains were smaller and more densely packed than in the fast PVP-capped mode described above (**Fig 2d, 2e**).

**Example 3. Gold (Au) patterns**

We have expanded the method of direct surface patterning to the deposition of other metals and non-metals using different precursor solutions.

5 Gold patterns were formed from tetrachloroaurate ( $\text{NaAuCl}_4$ ) solution prepared by adding 300 microliters of aqueous sodium carbonate solution (50mg/ml) to aqueous solution of gold tetrachloride acid trihydrate (30mg/400 microliters). The resulting solution (pH 8) was diluted with an equal volume of water and injected to the cell sample as in Example 1 above, to form gold patterns. **Fig. 3a** shows a deposited 3-4 micron width gold  
10 line. The morphology of the gold line was much denser than that of pure silver lines. EDS analysis showed pure gold (**Fig. 3b**) and lines were electrically conductive as the silver lines.

**Example 4. Copper oxide patterns**

15 A solution of diamminecopper hydroxide ( $\text{Cu}(\text{NH}_3)_2\text{OH}$ ) was prepared by dissolving copper sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , 1.5 gr.) together with sodium chloride ( $\text{NaCl}$ , 0.5 gr) in hot water (6 ml), and adding to a solution containing sodium bisulfite ( $\text{NaHSO}_3$ , 0.5gr) in 5 ml 5% sodium hydroxide aqueous solution. The white precipitate of cuprous chloride was washed with water by decantation, dissolved by  
20 ammonium hydroxide aqueous solution (10ml, 25%), passed through a 0.2 micron filter, and injected to the sample cell, as in Example 1 above to form patterns of copper oxide. **Fig. 4a** shows a deposited 4-micron width copper oxide line. **Fig. 4b** shows elemental composition of a copper oxide line examined by EDS.

In the same manner, an oxidized copper pattern of 4 microns width was obtained  
25 from an ammoniac aqueous solution of diamminecopper hydroxide  $\text{Cu}(\text{NH}_3)_2\text{OH}$  (Vogel, 1989). In this case EDS showed both copper and oxygen species, indicating a copper oxide though it is not possible to distinguish stoichiometry. These lines were formed with liberation of heat as for Ag and Au, but were electrically non-conductive, suggesting that oxidation occurred in the solution during pattern formation.

**Example 5. Molybdenum disulfide patterns**

30 A non-metallic pattern of molybdenum disulfide ( $\text{MoS}_2$ ) was formed in a similar manner by applying the laser to an aqueous solution of ammonium tetrathiomolybdate

(NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> (Walton et al., 1998; Wang et al., 1997). Line width was 3.5 to 7 microns and the morphology by SEM showed a spongy solid (**Fig. 5**). As EDS gives only elemental analysis, in this case the molecular identity of the final product was verified by Raman spectroscopy. The spectrum matches that of a MoS<sub>2</sub> standard, as well as published data (Frey et al., 1999). Unlike the case of metals, in which the solution appeared homogeneous even under observation using Nomarski differential interference contrast optics, the formation of MoS<sub>2</sub> deposits was clearly mediated by accumulation of preformed colloids at the laser focus. The deposition was also accompanied by liberation of heat and formation of vapor bubbles. Again, this is consistent with the semi-conducting nature of MoS<sub>2</sub>, with a bandgap of 1.1 eV, where the product absorbs the incident laser radiation having higher photon energy.

## Discussion

The infrared laser photons do not have sufficient energy to break chemical bonds. Thus the mechanism appears to be different from that reported for the photodeposition process (Weiss et al., 1992, 1994; Peled et al., 1992a, 1992b), where blue-green to UV laser light was used and the efficiency of the process diminished greatly with increasing wavelength. Suspended particles were also trapped by a convective flow (Shivashankar and Libchaber, 1998), which has in common with the present invention the use of an infrared laser in an “optical tweezers” configuration. In contrast to the present invention, preformed colloids of the final product were used as precursors in those prior art experiments.

Two apparently independent phenomena are required in the laser-induced deposition process: initiation and propagation. The similarity of the setup to that of “optical tweezers” suggests that collection and aggregation of preexisting particles. However, a fresh filtered diamminesilver hydroxide solution contains almost no suspended colloid as observed by the extremely sensitive differential interference contrast imaging. Some colloidal particles were observed at very low density in aged solutions. Still, however, bulk aggregation was not induced by operating the laser. Thus for the metal salts this seems not to be the relevant mechanism of initiation. First, we never observe initiation in the bulk of the solution, when the laser focus is more than about one micron from the substrate-solution interface. Second, when we prepared a suspension of silver colloids in advance and tried to initiate the deposition from it, in analogy with the heat induced convective flow method (Shivashankar and Libchaber, 1998), collection and aggregation took place only when the

colloid concentration was sufficiently high to make a visibly cloudy solution. In this case the line morphology was of spherical aggregates rather than the leaf-like structure observed for deposition from homogeneous precursor solution.

$\text{Ag}(\text{NH}_3)_2\text{OH}$  solution is well known as a precursor for producing silver mirrors, in which case the metal ion is normally reduced by a sugar or aldehyde at room temperature. We found that heating the  $\text{Ag}(\text{NH}_3)_2\text{OH}$  solution to  $80^\circ\text{C}$  for one hour, keeping the ammonia concentration constant, is also sufficient to induce an intramolecular redox reaction without any additional compound. The silver ion reduces to metal while the ammonium moiety is oxidized to hydroxylamine and nitroso derivatives.

For the case of silver as well as for the gold and the oxidized copper, we favor a mechanism of initiation by which a miniscule precipitate of the precursor itself adsorbs to the substrate. It serves to absorb enough of the laser radiation to start the deposition process by thermal decomposition. This is consistent with the increasing ease of initiation with time; a fresh solution usually does not yield a deposit immediately on application of the laser, while after approximately 20 minutes initiation of the deposit is most often instantaneous. To test this possibility, crystallites of solid  $\text{Ag}(\text{NH}_3)_2\text{OH}$  and  $\text{Ag}_2\text{O}$  (an intermediate compound in the synthesis of the former) were prepared and dried onto the glass surface. They were then rinsed with water and covered by the  $\text{Ag}(\text{NH}_3)_2\text{OH}$  ammoniac solution. In both cases the deposition began immediately when the laser was directed to one of the crystallites. When firmly attached to the glass surface, solid  $\text{Ag}(\text{NH}_3)_2\text{OH}$  was effective at lower laser intensities than  $\text{Ag}_2\text{O}$ , and we believe that it is the active initiator in practice.

The propagation itself appears to be thermal in origin. The laser incident on the metallic product generates Joule heating in the conduction electrons. The generated heat is confined to a small volume in which a temperature dependent reaction may be induced locally. The heat may be sufficiently intense to etch a borosilicate glass substrate. Thus once the process of deposition begins its propagation is self-sustaining. The width of the silver patterns is probably determined primarily by thermal diffusion, as a quickly drawn line may be much narrower than a spot produced by a stationary deposition. Also, the minimum widths attainable in all depositions accompanied by vapor formation are significantly larger than the diffraction-limited spot of the laser focus, of approximately 0.5 microns diameter. The same principle of a thermal reduction sustained by laser heating of the just-deposited product holds for the gold and copper patterns as well.

Nonetheless, the two modes observed for PVP-capped silver show that local heating is not a necessary factor for deposition from solution. In the absence of the thermal effect the deposition is many times slower to progress, and the minimum feature size is comparable to the diameter of the laser focus. Again the role of the surface deserves note,  
5 as focusing the laser in the bulk of the solution does not lead to a similar precipitation of the product.

In the case of  $\text{MoS}_2$ , the initiation stage does seem to follow the mechanism of collection and aggregation of existing colloids in the optical trap created by the focused laser. It has been shown previously that preparation of  $\text{MoS}_2$  from a solution of  $(\text{NH}_4)\text{MoS}_4$   
10 involves the formation of  $\text{MoS}_3$  as an intermediate. Heating to  $850^\circ\text{C}$  generates hexagonal  $\text{MoS}_2$  (Wang et al., 1997). Since the colloids we observe are created spontaneously in the concentrated  $(\text{NH}_4)_2\text{MoS}_4$  solution, they are likely to be composed of aggregates of  $(\text{NH}_4)_2\text{MoS}_4$  or  $\text{MoS}_3$ , whose formation does not require such extreme conditions as  $\text{MoS}_2$ . The next step involves the production of  $\text{MoS}_2$  from its deposited precursor, probably by  
15 local heating at the spot where the laser is focused. The  $\text{MoS}_2$  product is semiconducting and the laser energy is greater than the bandgap. Therefore, Joule heating occurs which is sufficient to boil the surrounding solution and to form vapor bubbles. The temperature rise is sufficient to melt or etch the glass substrate locally, and apparently to cause the transformation to  $\text{MoS}_2$  as well. Once  $\text{MoS}_2$  is formed it absorbs the laser radiation and the  
20 fast line formation is again self-sustaining.

The direct photodeposition method suggests number of applications in which it offers certain advantages to existing techniques for chemical surface patterning. First, it appears to be suitable to a broad range of materials, including molecular compounds such as  $\text{MoS}_2$  that are not amenable to simple vacuum deposition. As well, the change from  
25 deposition of one material to another is achieved simply by exchanging precursor solutions. Second, as a direct-write technique it can be applied quickly, with no overhead in mask production or photoresist chemistry. This should be particularly useful for prototype production, as well as for sample-specific labels such as serial numbers or codes. Of course, for mass production of identical units the conventional mask-based photolithography will  
30 be preferable. Third and perhaps most significantly, the deposits can be modified both during and after synthesis. Thus a pattern could be drawn and functionalized to saturation with one species, then another pattern drawn and functionalized with another species, and so on. In this way sequential steps can produce combinatorial arrays.



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**CLAIMS:**

1. A method for direct micropatterning of a surface by laser irradiation, which  
5 comprises:

(i) covering a surface with a sample comprises either a homogeneous solution of one or more soluble metal I salts or a suspension of a metal II-compound A;

(ii) irradiating the surface locally by applying a focused laser beam thus resulting in local deposition of either (a) a metal(s) I or metal I oxide(s) obtained from the  
10 decomposition of the metal I salt(s) from said homogeneous solution, or (b) a metal II-compound B obtained from the decomposition of the initial metal II-compound A from said suspension; and

(iii) repeating step (ii) by moving either the laser or the sample thus creating spots or lines of the deposited metal(s) I, metal I oxide(s) or metal II-compound B.  
15

2. The method according to claim 1, wherein said sample comprises a homogeneous solution of one or more soluble metal I salts.

3. The method according to claim 2, wherein said one or more metal I salts are soluble  
20 salts of a metal I selected for electrical conductivity or of a metal I serving as a basis for local adsorption or for modification by other chemical species.

4. The method according to any one of claims 1 to 3, wherein said soluble metal I salt is a salt of a metal I selected from Ag, Au, Pb, Ni and Cu.  
25

5. The method according to any one of claims 1 to 4, wherein said deposited metal I is silver.

6. The method according to claim 5, wherein said deposited silver is obtained from  
30 decomposition of  $\text{Ag}(\text{NH}_3)_2\text{OH}$ .

7. The method according to claim 5 or 6, wherein said deposited silver metal is further reacted with other chemical species.

8. The method according to claim 7, wherein said chemical species is hydrobromic acid thus resulting in a similar line of AgBr.

9. The method according to claim 7, wherein said chemical species is dithiothreitol,  
5 thus resulting in a similar line of silver complexed with sulfur.

10. The method according to claim 1, wherein said deposited metal I is gold.

11. The method according to claim 10, wherein said deposited gold is obtained from  
10 decomposition of NaAuCl<sub>4</sub>.

12. The method according to claim 1, wherein said deposited metal I oxide is copper oxide.

13. The method according to claim 12, wherein said deposited copper oxide is obtained  
15 from decomposition of Cu(NH<sub>3</sub>)<sub>2</sub>OH.

14. The method according to claim 12 or 13, wherein said deposited copper oxide is  
further reacted with dopants thus resulting in high temperature doped copper oxide  
20 superconductors.

15. The method according to claim 12 or 13, wherein said sample comprises a mixture  
of copper and dopant salts and the copper oxide is simultaneously deposited with the  
dopants thus resulting in high temperature doped copper oxide superconductors.  
25

16. The method according to claim 1, wherein said sample comprises a suspension of a  
metal II-compound A.

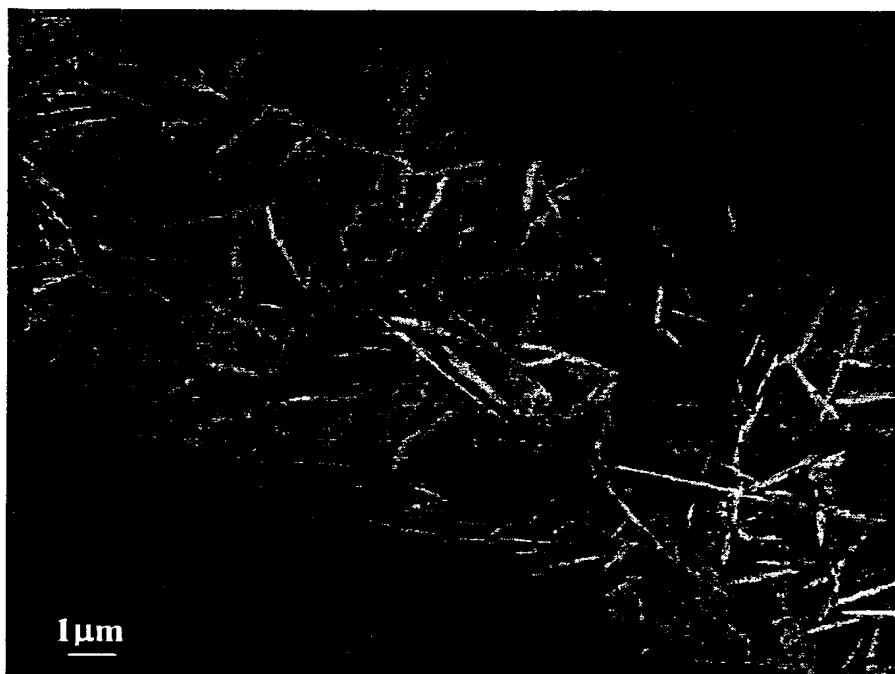
17. The method according to claim 16, wherein said metal II is a transition metal.  
30

18. The method according to claim 17, wherein said transition metal II is molybdenum.

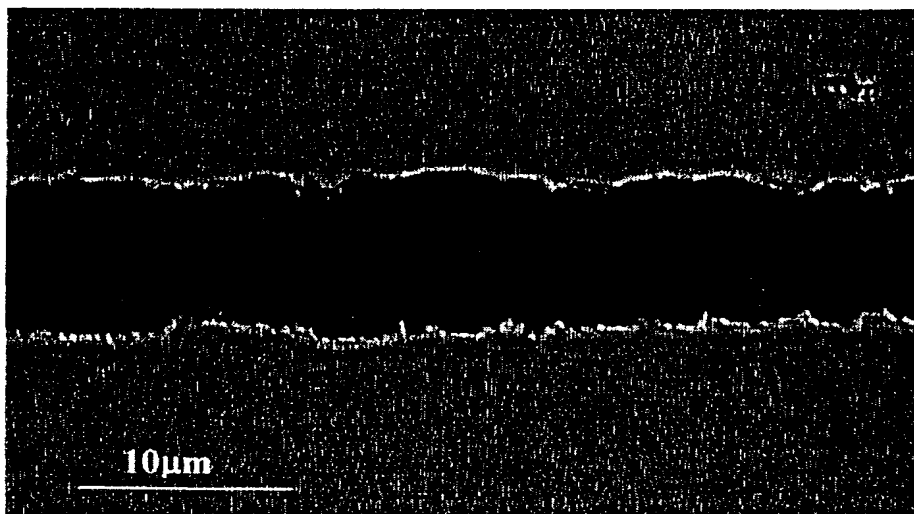
19. The method according to any one of claims 16 to 18, wherein said deposited metal II-compound B is  $\text{MoS}_2$ .

20. The method according to claim 19, wherein said deposited  $\text{MoS}_2$  is obtained by  
5 decomposition of the metal II-compound A  $(\text{NH}_4)_2\text{MoS}_4$ .

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**Fig. 1a**



**Fig. 1b**

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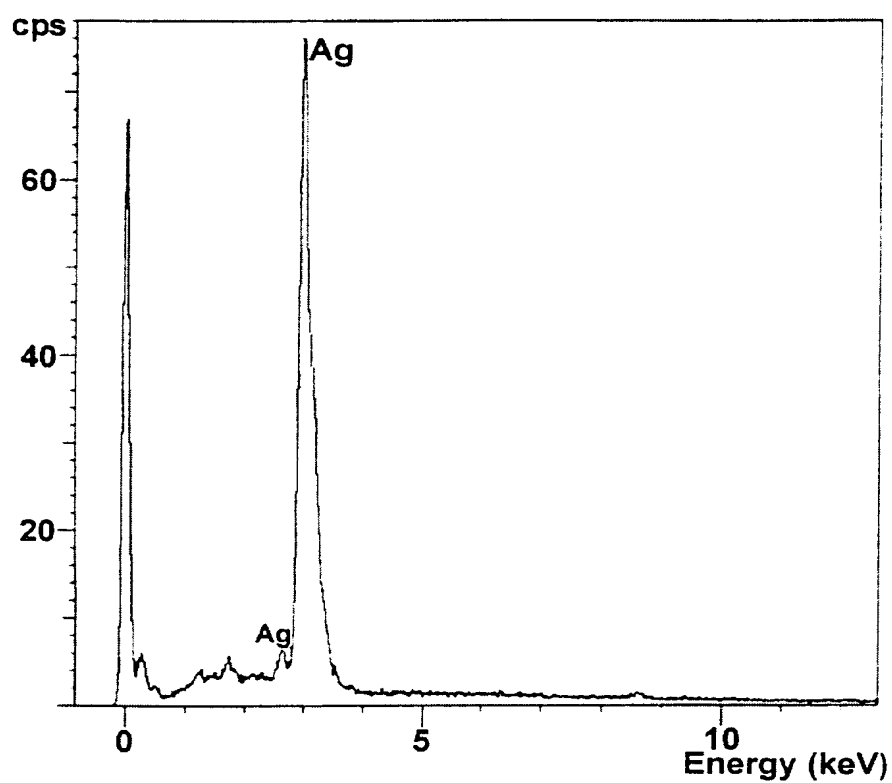


Fig. 1c

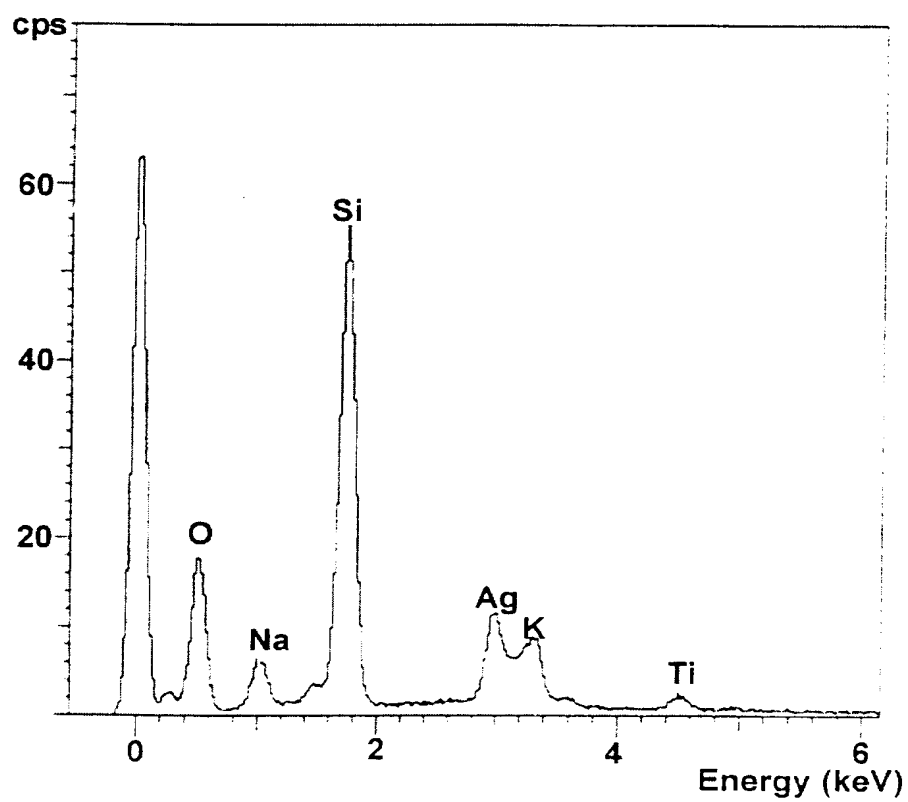


Fig. 1d

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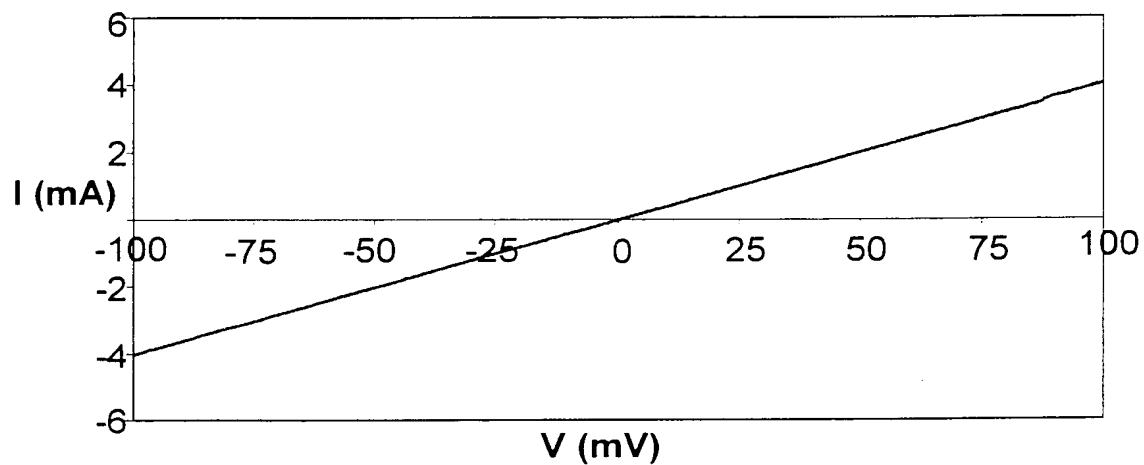


Fig. 1e

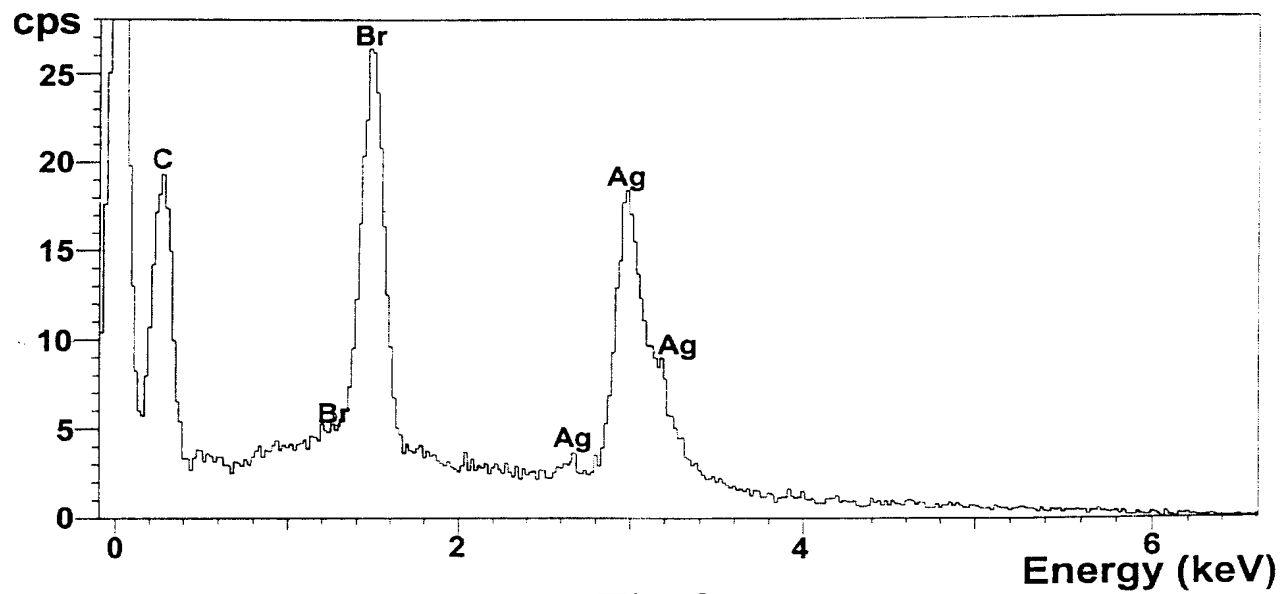
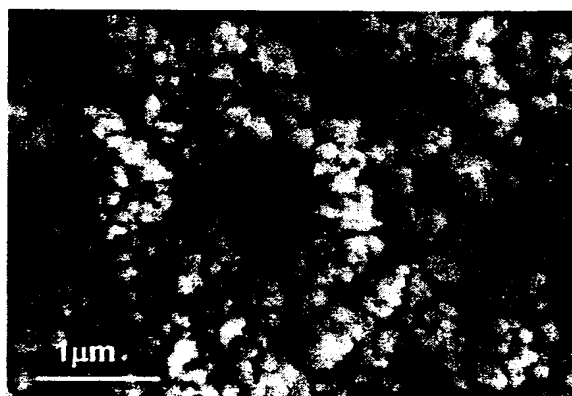


Fig. 2a

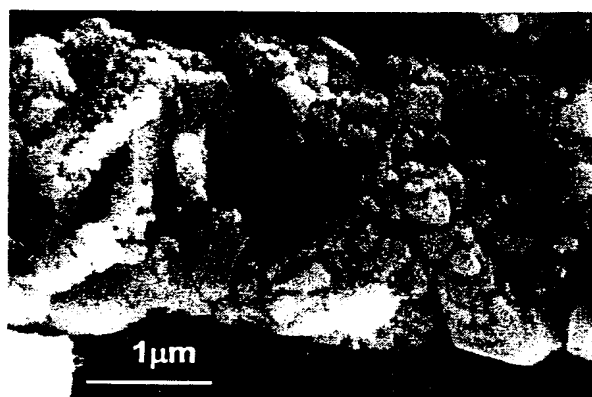
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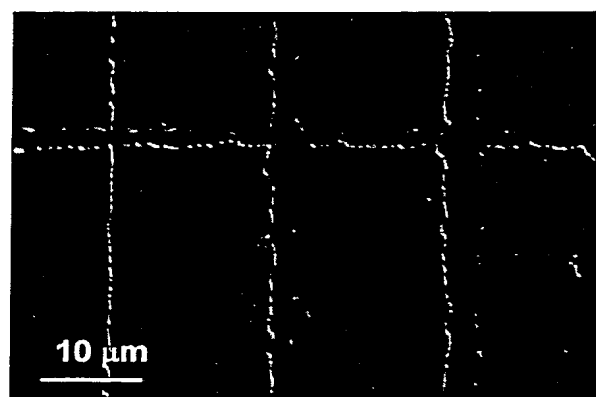
**Fig. 2b**



**Fig. 2c**



**Fig. 2d**



**Fig. 2e**



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Fig. 3a

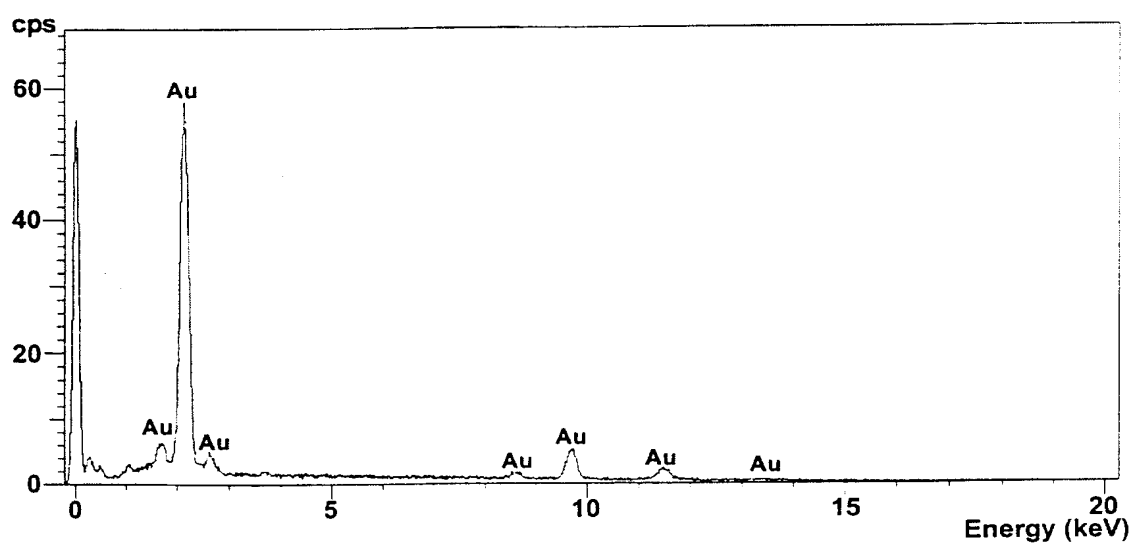


Fig. 3b

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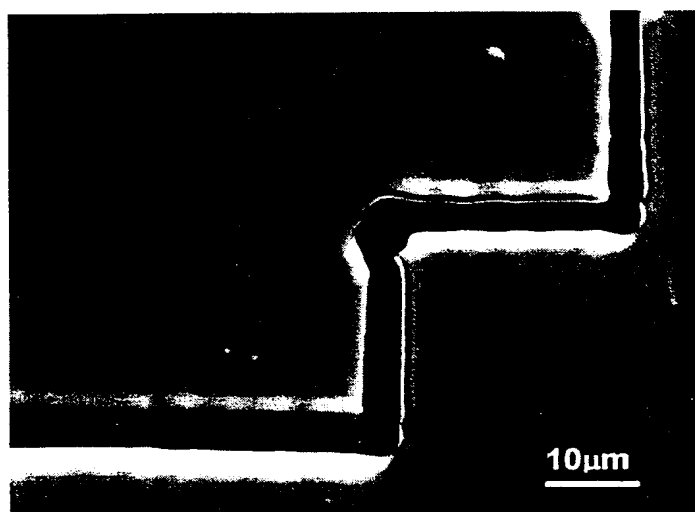


Fig. 4a

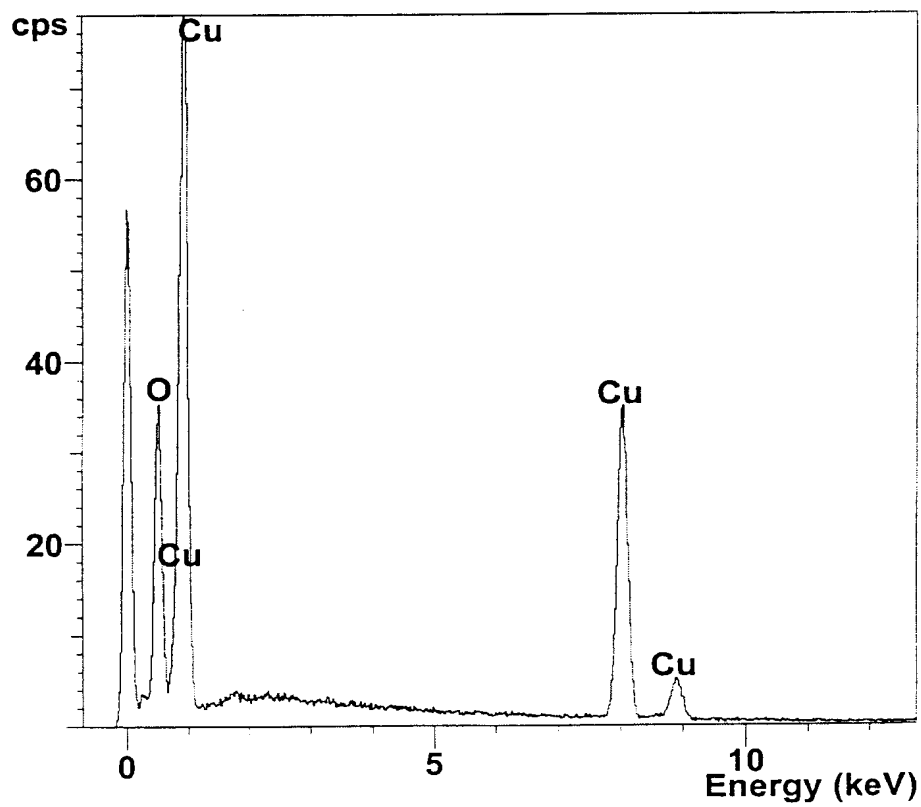
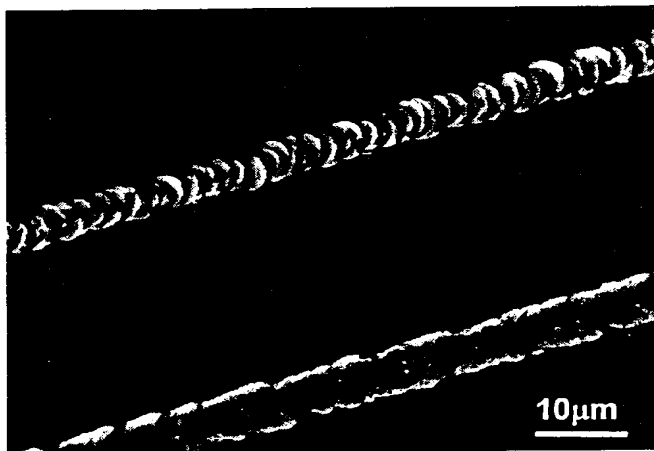


Fig. 4b

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**Fig. 5a**



**Fig. 5b**